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Serial No. 09/847,298   WALSDORFF et al.   PF 0000051416

closes spherical shapes (see column 6, lines 46-48) having the same disclosed surface area as Applicant's invention (see Final Rejection), which at least anticipates Applicant's recitation of a "powder form" in which no particular surface area is now claimed." For the sake of clarity applicants respectfully submit the following:

Convers et al. address at column 6, indicated lines 46 to 48 the oxychlorination process without giving any information on the surface area of the catalyst material.

Neither *Convers et al.* nor *Courty et al.* disclose data on the surface area of the catalyst particles. *Convers et al.* as well as *Courty et al.* in all instances address _specific_ surface areas, cf. the size of _all_ surfaces of the particle, including the surfaces of pores, holes etc., in relation to either the mass or the volume of the particle. A surface area per volume is mentioned only once[2], all other specific surface areas which are mentioned relate to the surface area per mass, expressed in m^2/g, ie.:

Convers et al. in **US 4,460,699**

- Col. 4, indicated lines 25 to 28: "A suitable range for low specific surface areas would be less than 50 m^2/g, but more preferably the specific surface area should be less than 25 m^2/g". Similar information is found in col. 12, indicated lines 16 to 20.

- Col. 4, indicated lines 62 to 67: "The carrier material used will have a high specific surface area, in the range of about 50 to about 300 square meters per gram, preferably from about 100 square meters per gram to about 200 square meters per gram (m^2/g), when it is dry and not disposed on the impeded center." Similar information is found in col. 12, indicated lines 24 to 27.

- Col. 7, indicated lines 58 to 61: "A ... sample of $1/4$" diameter alpha (α)-alumina spheres having a specific surface area of 15.5 m^2/g ...". Similar information is found in col. 8, indicated lines 19 to 22 and indicated lines 50 to 53.

- Col. 8, indicated lines 8 to 11: "Surface area of the finished catalyst was about 14.5 m^2/g and ...". Similar information is found in col. 8, indicated lines 40 to 43 and indicated lines 67 to 68, and in col. 9, indicated line 57.

- Col. 10, indicated lines 36 to 38: "Note that values in parenthesis on FIG. 5 represent the corresponding values of specific surface

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2) See col. 4, indicated lines 2 to 5, of **US 4,460,699**: The impeded center, considered by itself, should be large enough to deliver a packed, bulk geometric (external) surface area in the range of about 2-50 cm^2/cm^3 (including honeycomb catalyst monoliths).

area in meters squared per gram (m²/g)."

Courty et al.* in *US 4,381,415

- Col. 3, indicated lines 3 to 5: *"(a) an alumina carrier of a spe-cific surface higher than 50 m² per gram and, preferably higher than 80 m² per gram"*. Similar information is found in col. 3, indicated lines 29 to 31 and indicated lines 41 to 44; in col. 11, indicated lines 12 and 13, indicated lines 25 to 27 and indicated lines 36 to 38.

- Col. 3, indicated lines 61 to 63: *"... [the carrier] has a specific surface from 50 to 400 m²/g and preferably from 80 to 350 m²/g and ..."*.

- Col. 4, indicated lines 27 to 31: *"... consisting of balls having a diameter from 1.6 to 2.5 millimeters, a specific surface of 200 m²/g and ..."*. Similar information is found in col. 5, indicated lines 17 to 20, and in col. 6, indicated lines 42 to 45.

The _specific_ surface area of a particle includes "internal" surfaces, cf. surfaces of pores and holes within the particle[3], and information pertaining to the _specific_ surface area of a catalyst particle is, therefore, not indicative of the size of the catalyst particle. The Examiner's position that the catalyst powder and the process of mak-ing which is defined in applicants' claims is anticipated by *Convers et al.* and by *Courty et al.* because applicants' claims fail to speci-fy a *"surface area"*, cf. a specific surface area, which is different from the specific surface areas addressed in the prior art references is therefore deemed to be without merit.

With regard to the size and the shape of the catalyst particles, the following information is provided by the prior art references:

- col. 3, indicated line 58, to col. 4, indicated line 1, of *US 4,460,699*: *"For most commercial fixed bed processes ... sizes from about 1/8" to 3/8"[4] in average diameter will be used, ... The impeded center and the covering layer combined should approximately equal the size desired for the finished fixed bed catalyst. Impeded centers ... (for example spherical) ... should have average diame-ters in the range of about 1 mm to about 10 mm"*.

- Col. 7, indicated lines 58 to 61, of *US 4,460,699*: *"A ... sample of 1/4"[5] diameter alpha (α)-alumina spheres ..."*. Similar information is found in col. 8, indicated lines 19 to 22 and indicated lines 50 to 53.

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3) Compare, for example, *Le Page et al.* "Applied Heterogeneous Catalysis" pages 200 to 202, copy attached.

4) Corresponding to about 3 to 9 mm.

5) Corresponding to about 6 mm.

- Col. 4, indicated lines 27 to 31, of *US 4,381,415*: "*... consisting of balls having a diameter from 1.6 to 2.5 millimeters ...*".
- Col. 5, indicated lines 17 to 20, of *US 4,381,415*: "*... consisting of extrudates having a diameter of 1.2 mm, lengths from 4 to 7 mm ...*".
- Col. 6, indicated lines 42 to 45, of *US 4,381,415*: "*... consisting of balls having a diameter from 1.8 to 2.5 mm ...*".

In light of the size of the catalyst particles which is specified by *Courty et al.* and by *Convers et al.* the prior art catalysts are particulate and are clearly not in powder form.

In light of the foregoing and the arguments presented in applicants' previous paper it is therefore respectfully urged that neither the teaching of *Convers et al.* in *US 4,460,699* nor the teaching of *Courty et al.* in *US 4,381,415* anticipate the subject matter of applicants' Claims 2, 3, 5, 6 and 12 within the meaning of 35 U.S.C. §102. Favorable reconsideration of the Examiner's position and withdrawal of the respective rejections is solicited.

REQUEST FOR EXTENSION OF TIME:

A request for a *one* month extension of time and the requisite fee of *$110.00* is submitted with applicants' Notice of Appeal of even date with this paper.

Please charge any shortage in fees due in connection with the filing of this paper, including Extension of Time fees, to Deposit Account No. 11.0345. Please credit any excess fees to such deposit account.

Respectfully submitted,

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Encl.: *Le Page et al.* "*Applied Heterogeneous Catalysis*" pp. 200 to 202
HBK/BAS

Institut français du pétrole publications

J.-F. LE PAGE, J. COSYNS, P. COURTY
E. FREUND, J.-P. FRANCK
Y. JACQUIN, B. JUGUIN, C. MARCILLY
G. MARTINO, J. MIQUEL, R. MONTARNAL
A. SUGIER, H. VAN LANDEGHEM

Institut Français du Pétrole

applied heterogeneous catalysis

design · manufacture use of solid catalysts

Foreword by
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Director of Refining and Petrochemicals, 1964-1979
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Currently Director of École Nationale Supérieure
du Pétrole et des Moteurs

These results for the catalyst for oxidizing methanol into formaldehyde were confirmed later by S. PEIRS (Ref. [10]), who also showed that Raman spectrometry of this family of catalysts supported results obtained by the preceding methods.

7.3. TEXTURE OF A CATALYST

Heterogeneous catalysis is a surface phenomenon; and it is not enough for the ideal catalyst simply to have the required elementary composition formed during preparation and start-up. There must also be the largest possible active surface for any given mass of catalytic agent and this active surface must be topographically arranged through an optimized pore distribution so as to facilitate the access of reactants and the departure of products, in other words, in such a way as to limit diffusional phenomena as much as possible. Therefore, we are going to examine the following characteristics:

(1) The total specific area of a catalyst.
(2) The dispersion of the active agents: size of aggregates and crystallites and gradients of dispersion inside the grains.
(3) The pore distribution on which the intragraular diffusional phenomena depend.

7.3.1. The total specific area of a catalyst

The external surface is negligible compared to the internal surface comprising the walls of the pores, which are considered to be cylindrical as a first approximation; and it was seen in Chapter 5 that the size of the surface can be approximated by the following relation:

$$S = \frac{4V_{PT}}{\Phi}$$

where

S = specific area of the catalyst ($m^2 \cdot g^{-1}$),
V_{PT} = total pore volume ($cm^3 \cdot g^{-1}$),
Φ = average diameter of the pores.

Application of this formula, which is only approximate, requires the prior determination of V_{PT} and Φ.

In practice, the method most used for determining specific area is the BET method (BRUNAUER, EMMETT and TELLER) based on the physical adsorption of an inert gas at constant temperature, usually nitrogen at the temperature of liquid nitrogen. The principle of measurement consists in determining the point when a mono-molecular layer of gas covers the surface of the catalyst, as shown in Fig. 7.10. If this layer corresponds to the quantity V_m, for a gas whose molar volume is V_M, the surface of the sample studied will be written:

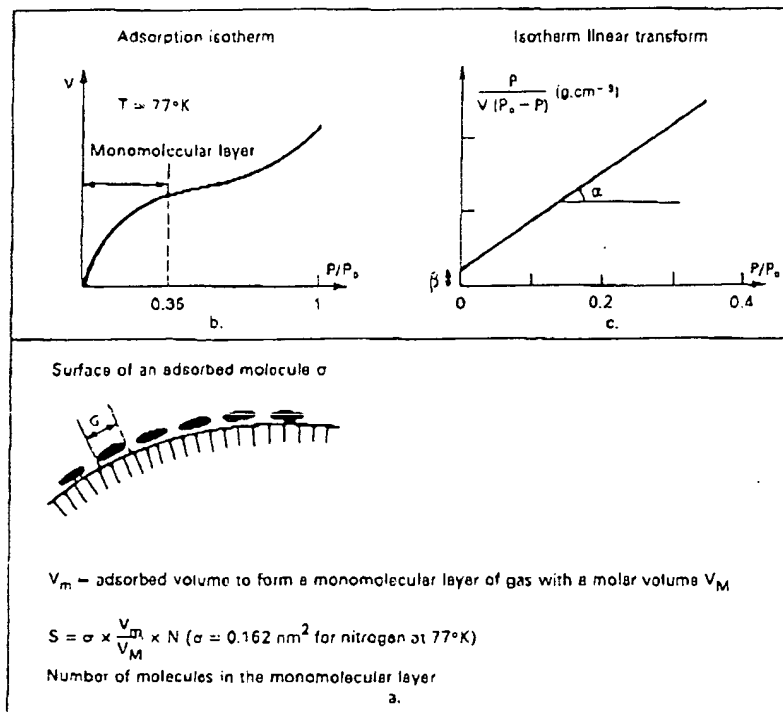$$S = \sigma \cdot \frac{V_m}{V_M} \cdot N_A$$

FIG. 7.10   Determining specific surface through physical adsorption of a vapor, generally nitrogen at 77K.

(a) Schematic representation of the adsorption. (b) Adsorption isotherm: $V = f(P/P_0)$. (c) Linear transform of the isotherm on the basis of the Brunauer, Emmett and Teller, (BET) model for relative pressures P/P_0 between 0.05 and 0.35.

$$PV(P_0 - P) = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0}$$

V = the volume of gas adsorbed by 1 g of solid under pressure P. V_m = the volume necessary to form the monolayer. C = a physical constant characteristic of the gas-solid system and depending on the heat of adsorption, Q_1, of the vapor on the solid, and on the latent heat of liquefication of the same vapor, Q_2, according to the equation:

$$C = \exp\left(\frac{Q_1 - Q_2}{RT}\right)$$

The slope, α, of the straight line and its ordinate, β, at $P/P_0 = 0$ are used to determine the values of V_m and C, as follows:

$$V_m = \frac{1}{\alpha + \beta} \quad ; \quad C = \frac{\alpha}{\beta} + 1$$

Knowing V_m one can then determine S (BET method). If the vapor is nitrogen at 77° K, $S_{BET} = 4.37 V_m$.

where σ is the area covered by the adsorbed molecule, and $\left[\dfrac{V_m}{V_M} \cdot N_A \right]$ the number of molecules constituting the single layer when N_A is the Avogadro number.

Experimental methods used for determining V_m are numerous and described at length in specialized articles (Refs [11, 12, 13, 14]). We are limited here to noting that the most frequently used methods are thermogravimetry, volumetry and sorptometry.

It must be pointed out that the specific area of catalysts with small surfaces can advantageously be derived from the pore distribution curve obtained through mercury porosity measurement, as will be seen later. The specific area can also be estimated through measuring the dimensions of the catalyst particles by X-ray diffusion or diffraction (diffusion at small angles or broadening of the X-ray diffraction lines).

In the case of bulk catalysts composed solely of active agents, the total specific area can be taken as the measure of the active specific area; this is not the case, however, if the catalyst is supported, since the support plays the role of dispersing agent, diluent or binder. But even in this latter case knowledge of the total surface of the active agent (or of the support) can still be useful, if only for judging the dispersing role of the support in relation to the active agents during the impregnating operation, as shown in Fig. 7.11.

7.3.2. Dispersed state of the active agents

When the active species are supported or diluted, there is no longer a direct relation between the total specific area and the observed catalytic performances, particularly the activity; and it is necessary to determine the available active surface, i.e., the number of molecules or atoms of active agents accessible to the reactants. Defined in this way, the characteristic designated as "active specific surface" remains an overall characteristic in the sense that all the atoms or molecules making up the active surface are considered as equivalent from the point of view of their catalytic properties. The actual case is generally more complicated; it is reasonable to think that the various atoms of a nickel crystallite, for example, offer different catalytic activities for certain reactions according to their different coordination indices, depending on whether they are situated on the corners, the edges or the different planes of the crystallite (Figs 1.6 and 1.7). Consequently, correlations between the catalytic properties and the surface of active agents are only a rough interpretation of the catalytic phenomena. Nevertheless such correlations hold some interest, as will be shown in the course of describing current methods of measuring surfaces of active agents by some examples relative to industrial catalysts.

7.3.2.1. Chemisorption

Contrary to physical adsorption, which precludes differentiating between support and active agent, chemisorption is generally specific (Figs 5.1.5 and 1.9). The method of measurement consists of adsorbing on the surface atoms of the active agent a compound capable of a complete surface reaction leading to the formation of a single chemisorbed layer of molecules; the measurement of the adsorbed quantity then indicates the state of dispersion of the active agent.

This method is frequently used when the active agent is a metal the nature of which dictates the chemisorbed molecule as well as the conditions of chemisorption. The number